

DEGRADATION OF DISLodgeABLE RESIDUES OF
AZINPHOS-METHYL FOLLOWING APPLICATION
TO APPLE TREES

by

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SUMMARY

In May and June 1983, five apple orchards treated with azinphos-methyl (Guthion 50W) were monitored to determine the degradation rate of dislodgeable residues on the foliage. Leaf punch samples were collected periodically for 28 days. This study was conducted to evaluate the 14-day reentry interval now required by regulation in California. Animal studies to determine a dermal dose-response curve, as well as the dislodgeable residue degradation curve, were used to determine the time when workers may reenter the orchard with minimal hazard. The safe levels on foliage have been calculated to be 1.6 ug/cm^2 for azinphos-methyl and its oxon. Under the conditions that existed in these five groves and at the application rate used, the average foliar residues were below 1.6 ug/cm^2 by day seven. The oxon was not found in any sample collected from these orchards.

INTRODUCTION

Azinphos-methyl (Guthion^R) is a Toxicity Category I organophosphate insecticide. This chemical has an oral LD₅₀ (rat) of 11-13 mg/kg and a dermal LD₅₀ (rat) of 220 mg/kg (1). During the past 25 years, a number of pesticide-related illnesses of field workers in California have been attributed, at least in part, to dermal exposure to residues of azinphos-methyl on the leaf surface (2). The severity of the resulting illnesses was presumed to be dependent on the amount of residue on the leaf surface and the extent and duration of contact with the leaf (3). Another source of exposure could be contact with contaminated soil particles on the orchard floor (4). (Soil contamination was not addressed in this study.)

The California Department of Food and Agriculture (CDFA) establishes reentry intervals to protect field workers from excessive exposure to high residues on crops. The reentry intervals that went into effect more than 15 years ago were often supported by a very limited data base. This study was conducted to determine the degradation rate of azinphos-methyl on apple foliage. Dermal dose-response studies in laboratory animals by Knaak, et al., (5, 6), and controlled human testing by Richards, et al., (7), have been used to calculate "safe levels" of residue on foliage. This calculated safe level is theoretically, the amount of residue on the foliage that will not result in significant cholinesterase depression when the worker comes into contact with it for long periods of time. The dermal dose-response data along with the degradation data can be used to determine the reentry interval.

Azinphos-methyl is registered for use on a wide variety of fruit, vegetable, and nut crops to control numerous insects. In 1982, a total of 543,675 pounds of azinphos-methyl were reportedly applied in California (8). The major uses were almonds, celery, ornamentals, peaches, and walnuts (> 20,000 pounds each).

MATERIALS AND METHODS

Six apple orchards in Santa Cruz County were selected for this study. One orchard was used as a control and was not treated with azinphos-methyl. Sampling rows were selected and marked and one set of samples was collected prior to treatment. The identified orchards were treated in the following manner:

Equipment: Speed sprayer (pulled by track-laying tractor).

Chemical of

Interest: 4 pounds Guthion 50W/500 gallons water/1.25 acres [equals 1.6 pounds active ingredient (a.i.) /acre in 400 gallons water].

Other

Chemicals

in Tank Mix: Dikar (mancozeb and karathane), K-27 spreader, Urea.

Samples were then collected at 24 hours, 48 hours, 72 hours, 6-7 days, 14 days, 20-21 days, and 27-28 days post-application. The control orchard was sampled in the same manner and on the same days as the treated orchards.

Foliar samples were collected using methods described by Gunther, et al., (9) and Iwata, et al., (3). Each sample consisted of 40 leaf discs, each 2.54 cm in diameter. The sampling strategy was as follows:

Each field was divided into three equal areas. The middle row from each area was marked. Leaf punches were collected from 10-20 trees (depending on the length of the rows) in each selected row. The first 3 to 4 trees in each row were not sampled. Leaf discs were randomly collected from all sides of the trees. The samples were then sealed with aluminum foil, capped, and stored on ice until delivered to the Worker Health and Safety Unit's chemistry laboratory in Sacramento.

Each sample was analyzed for dislodgeable residues of the parent compound and the oxon. Azinphos-methyl residues were extracted from the leaf surface with a water/surten solution and extracted from the water with dichloromethane. Analysis was done by gas liquid chromatography equipped with an NP detector. The analytical methods can be found in Appendix 1.

RESULTS AND DISCUSSION

Dermal dose-response information on azinphos-methyl has been established by Richards, et al., (7), and Knaak, et al., (5, 6). Safe levels of azinphos-methyl residue on foliage have been calculated to be 1.6 ug/cm² for the parent compound and the oxon. Average dislodgeable residues of azinphos-methyl found in the five treated orchards are in Table 1. The oxon of the parent compound was not found at any time during this study. At the application rate used for this study, average residues of the parent compound found after 24 hours were approximately 2.4 ug/cm². The residues decreased rapidly until at 7 days after application the levels were below the "safe level" of 1.6 ug/cm² calculated for azinphos-methyl and its oxon.

According to the label, the amount of actual azinphos-methyl applied per acre depends upon the amount of water used to make a "full coverage spray." The label rate is as follows: 1/2 to 5/8 pounds Guthion 50% in 100 gallons of water as a full coverage spray using not more than 1,000 gallons of finished spray per acre. Thus, the label allows up to 3.125 pounds a.i. per acre in 1,000 gallons of water. In this study, 400 gallons of water was used; thus, the label dilution rate would be 1.0 to 1.25 pounds a.i. per acre. There is a sentence on the label that states, if less than maximum volumes of water are used, the concentration of Guthion 50% could be increased in order to apply the same amount as when more water is used. Thus, even though the label states to use 1.25 pounds a.i. per acre in 400 gallons, the statement above would allow up to 3.125 pounds a.i. per acre in order to obtain the higher dose as would be found in the full coverage spray for 1,000 gallons of water.

In studies conducted by Knaak and Iwata (6), azinphos-methyl applied to citrus trees at rates up to two pounds a.i. per acre, did not break down to form the more toxic oxon. The oxon was found in studies they conducted that involved the application of six pounds a.i. per acre. Dry, hot environmental conditions have been shown to be a factor in the formation and persistence of paraoxon (following application of parathion)(10). Presumably, the same holds true for the development of the oxon of azinphos-methyl. Apples tend to be grown in areas with generally cool climates, thus, at lower application rates, formation of azinphos-methyl oxon would not be expected.

Under the conditions of this study, foliar residues would have allowed reentry into these five orchards with minimal hazard seven days after application of the pesticide. Residue levels in the soil under the trees were not studied. There can be considerable run-off spray with consequent surface soil contamination when high gallonage rates are used.

RECOMMENDATIONS

The 14-day reentry interval, required by California regulations, might have been longer than necessary for this low application rate and cool, damp climate. According to data developed in this study, the reentry interval might be reduced for application rates of 1.6 pounds a.i. per acre or less. For higher application rates, the reentry might need to remain at 14 days. This issue needs further study.

It is possible that if hot, dry environmental conditions exist for one or more days, significant oxon formation might occur and thus, create a worker reentry hazard. This issue needs to be studied further.

Table 1

Average Dislodgeable Guthion Residues on Apple Foliage

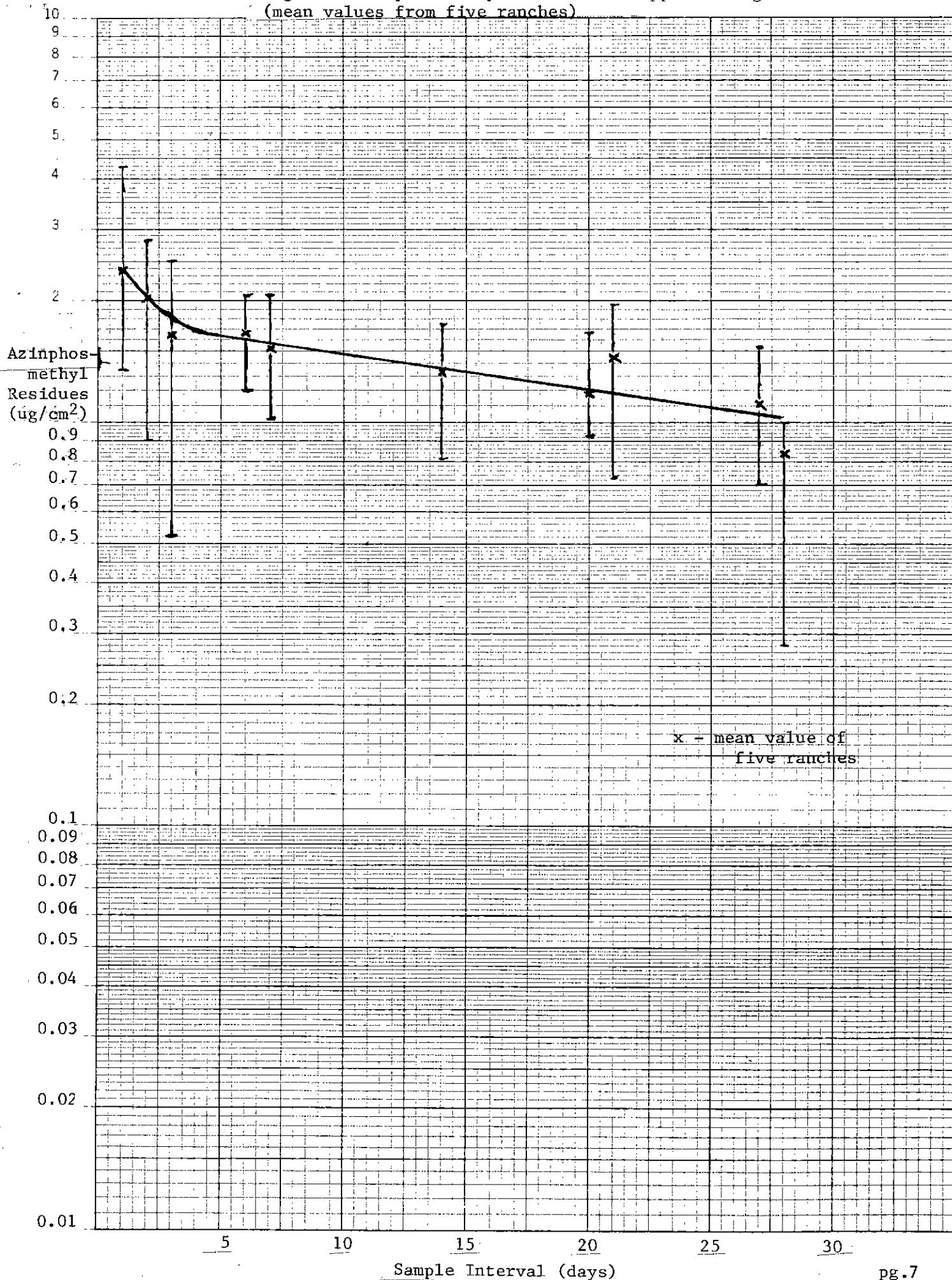
<u>Sample Interval</u>	<u>Guthion Residue (ug/cm²)</u>	<u>Guthion Oxon Residue (ug/cm²)</u>
Presample	ND	ND
24 hours	2.39 + 0.78	ND
48 hours	2.02 + 0.65	ND
72 hours	1.64 + 0.55	ND
6 days	1.68 + 0.32	ND
7 days	1.52 + 0.36	ND
14 days	1.34 + 0.30	ND
20 days	1.18 + 0.28	ND
21 days	1.44 + 0.41	ND
27 days	1.11 + 0.31	ND
28 days	0.84 + 0.20	ND

Table 2

Weather Conditions for the Watsonville Area During the Course of This Study (collected by the National Weather Service).

Temperature (°F)				
Date	Maximum	Minimum	Rainfall (Inches)	Notes
May 15	67	52		Orchards sprayed
16	75	45	No measurable rainfall occurred during the study period.	
17	76	47		
18	83	49		
19	82	51		
20	85	54		
21	74	54		
22	69	53		
23	68	54		
24	67	55		
25	69	51		
26	68	52		
27	69	53		
28	69	54		
29	66	55		
30	72	48		
31	75	55		
June 1	69	55		
2	62	54		
3	65	54		
4	65	53		
5	70	53		
6	77	53		
7	81	55		
8	65	56		
9	64	55		
10	70	54		
11	72	50		
12	72	49		
13	74	49		
14	86	52		
15	74	52		
Average	71.9	52.4		
Average Daily Temperature 62.1				

FIGURE 1: Dislodgeable Azinphos-methyl Residues of Apple Foliage
(mean values from five ranches)



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Original Date: 7-29-83
 Supersedes:
 Current Date: 7-29-83
 Method #: 27.0

DETERMINATION OF DISLODGEABLE GUTHION FROM LEAF PUNCHES.

SCOPE:

This method is for analyzing dislodgeable Guthion from leaf punches.

PRINCIPLE:

Guthion (o,o-dimethyl-s-(4-oxobenzotriazino-3-methyl) phosphorodithioate) is extracted from leaf punch surfaces by using water and surten solutions. Accumulated water is extracted with Dichloromethane (DCM). DCM is evaporated to dryness and made to volume in ethyl acetate. Analysis is done by a GLC equipped with NP detector.

REAGENTS AND EQUIPMENT:

Gas Liquid Chromatograph (Varian 3700) equipped with auto sampler and NP detector. Rotary evaporator with water temp. set at 30 degrees.

Tumbler

Glassware as needed

Dichloromethane nano grade

Ethyl Acetate nano grade

Surten diluted 1s to 50ml.

ANALYSIS:

Add 50 ml of distilled water and 4 drops of diluted surten solution into the Jar containing leaf punches. Secure the lid tightly. Make sure to have enough layers of aluminium foil in between the glass Jar and the lid to avoid any leak. Tumble the Jar for 30 minutes at 30 rpm, decant water into a 500 ml separatory funnel. Repeat the process two more times.

Extract the accumulated water with 2 x 50 ml portions of DCM. Drain DCM through a bed of anhydrous sodium sulfate. Evaporate DCM on a rotary evaporator to dryness. Make volume in ethyl acetate and analyze by GLC.

EQUIPMENT CONDITIONS:

COLUMN	4% OV-1 on 100/120 Gaschrome G in 3 ft. x 2mm glass column
OVEN TEMP.	220 degrees
DETECTOR	NPD
CARRIER GAS	Nitrogen at 30 ml/min.
CHART SPEED	.5 cm/min
RANGE	1x1
RT.	8.74 min.
INJ. TEMP	230 degrees

CALCULATIONS:

$$\text{Guthion (us/cm}^2\text{)} = \frac{\text{Pk.ht.sample} \times \text{ns std.injected} \times \text{conc.factor}}{\text{Pk.ht.std.} \times \text{ul sample injected} \times \text{surface area leaf punches}}$$

DISCUSSION:

The system was found to be linear in the range of 0.38 ns to 18.88 ns. Linearity was not checked beyond 18.88 ns. Guthion D.A was not detected under the conditions and was analysed on HPLC. Minimum detectable level on 40 punches was .01 us/cm².

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Supersedes:
Current Date: 7-29-83
Method #: 53.0

DETERMINATION OF DISLODGEABLE ZOLONE AND ZOLONE O.A.

NOTE: For principle, method of extraction, equipment conditions and method of analysis see "Guthion method # 27.0"

RETENTION TIMES:

Zolone O.A= 4.80 min
Zolone = 6.84 min
Guthion = 8.74 min

DISCUSSION

System is linear for Zolone O.A. from 4 ng to 40 ng and for Zolone from 2 ng to 20 ng injected. MDL from 40 leaf punches for Zolone O.A is .02 ug/cm² and for Zolone is .01 ug/cm².

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